Phase equilibria of the Al-Cu-Zn system for compositions close to brass alloys

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Abstract

The effect of aluminium in the equilibrium phases of the Cu-Zn alloys, within the range of chemical compositions of interest to brass producers, has been studied. Ternary alloys were casted by melting two Cu-Zn base alloys (with ~59.5% and ~61.2 wt.% of Cu) followed by the addition of aluminium up to 3.68 wt.%. Isothermal homogenization, followed by rapid cooling, has been employed to determine the equilibrium phases at different temperatures. The alloys have been observed by scanning electron microscopy (SEM) and the respective chemical analysis determined by electron probe microanalysis (EPMA). The statistical analysis of the obtained results enable to correlate the chemical composition of equilibrium phases with temperature, for the range of compositions studied.

Introduction

Although brasses are essentially alloys of copper and zinc, they also contain some alloying elements which are responsible for a wide variety of properties and applications of these materials. Aluminium is one of the most common elements present in the composition of brasses (in the range of 0.2 to 0.7 wt%) namely in cast brasses produced by die casting [1933Vic, 1952Kli, 1957Bil, 1959Tho, 1968INI, 1983CTI].

Its presence is necessary to promote deoxidation and castability, to reduce zinc evaporation and to protect the melt from the oxidation at high temperatures. Aluminium is also responsible for the improvement of corrosion and erosion resistance of the alloys, which enables the use of aluminium brasses in heat exchangers [1952Kli, 1956Fre, 1978But, 1995Loc, 1983CTI, 1987ASM, 1988Ric, 1992Fas, 1995Dio, 1998Bec]. In addition, this element increases the volume fraction of β phase in the microstructure of brasses and improves the mechanical resistance of the alloys [1984Web, 1995Dio, 1999Vil1]. The range of chemical compositions close to brass alloys has been studied by Bauer *et al* in 1932 [1932Bau]. According to these authors, the presence of aluminium in brasses modifies the existing equilibrium phases. Bauer *et al* [1932Bau] have studied the Al-Cu-Zn system, using thermal analysis and metallographic techniques, and determined the vertical sections of this system for 1, 2, 4 and 6 wt% of aluminium content and for copper contents between ~45 and 90 wt.%. In the present work, the equilibrium phases and its chemical composition have been determined for Al contents up to 3.68 wt.% for two base alloys with different copper contents. The chemical compositions of the obtained equilibrium phases, at different temperatures, have been determined by EPMA.

Several isothermal sections of the ternary phase diagram, obtained from results of several authors, were compiled by Villars *et al.* [1997Vil].

Experimental procedure

Two base alloys Cu-Zn, of ~59.5 wt. % and ~61.2 wt. % Cu, were prepared by melting high purity copper and zinc (≥ 99.9% purity) in a medium frequency (3000 Hz) induction furnace. These alloys were remelted to obtain alloys with different Al contents, in the range of 0 to 3.68 wt.%. All the alloys were poured in a steel mould.

Specimens were cut from each alloy and analysed by XRF spectrometry to determine their chemical compositions. The resulting alloys were homogenized at different temperatures, 650, 550, 450 and 350 ºC in a heat treatment furnace. A type K thermocouple was used to measure temperature, with an accuracy of ± 1.5ºC.The samples were first heated up to 830 ºC and then slowly cooled to the homogenization temperature. After a stage of 24 hours at each temperature, to assure fully homogenization, samples were rapidly quenched in a solution of salted water, with 50g/l NaCl, and ice at ~0ºC. The thermal cycle is presented on figure 1.

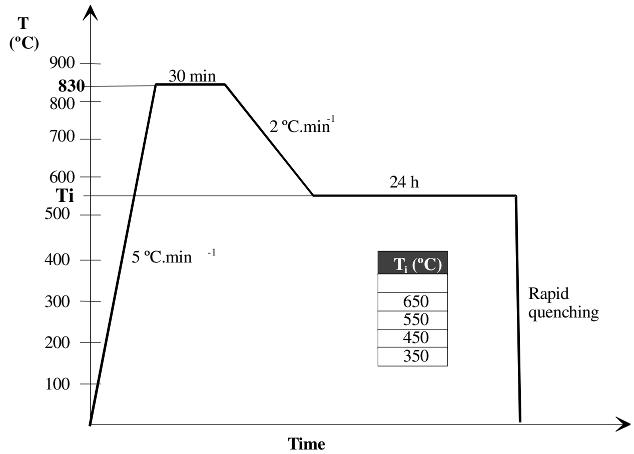


Figure 1 - Thermal cycle used in the homogenization experiments.

After the homogenization experiments, the alloys were observed in a scanning electron microscope (SEM), JEOL JSM35C, and the chemical compositions of the phases determined by electron probe microanalysis (EPMA), CAMECA SX 50.

Results and discussion

The chemical compositions of the alloys produced in this work are presented in table 1.

Table 1 - Chemical compositions of the alloys produced in this work (wt. %).

Alloy nº	Cu	Zn	Al
1	59.55	40.45	< 0.05
2	61.24	38.76	< 0.05
3	61.33	38.18	0.49
4	61.04	37.91	1.05
5	60.82	37.58	1.60
6	61.35	35.28	3.37
7	59.63	39.83	0.54
8	59.38	39.53	1.09
9	59.43	38.99	1.58
10	58.72	37.60	3.68

No detectable amounts of other elements were found.

The addition of Al to the base alloys strongly modifies the microstructures concerning the present phases as well as their volume fraction. Figure 2 illustrates the modifications in the microstructures of the base alloy nº2 caused by the Al addition.

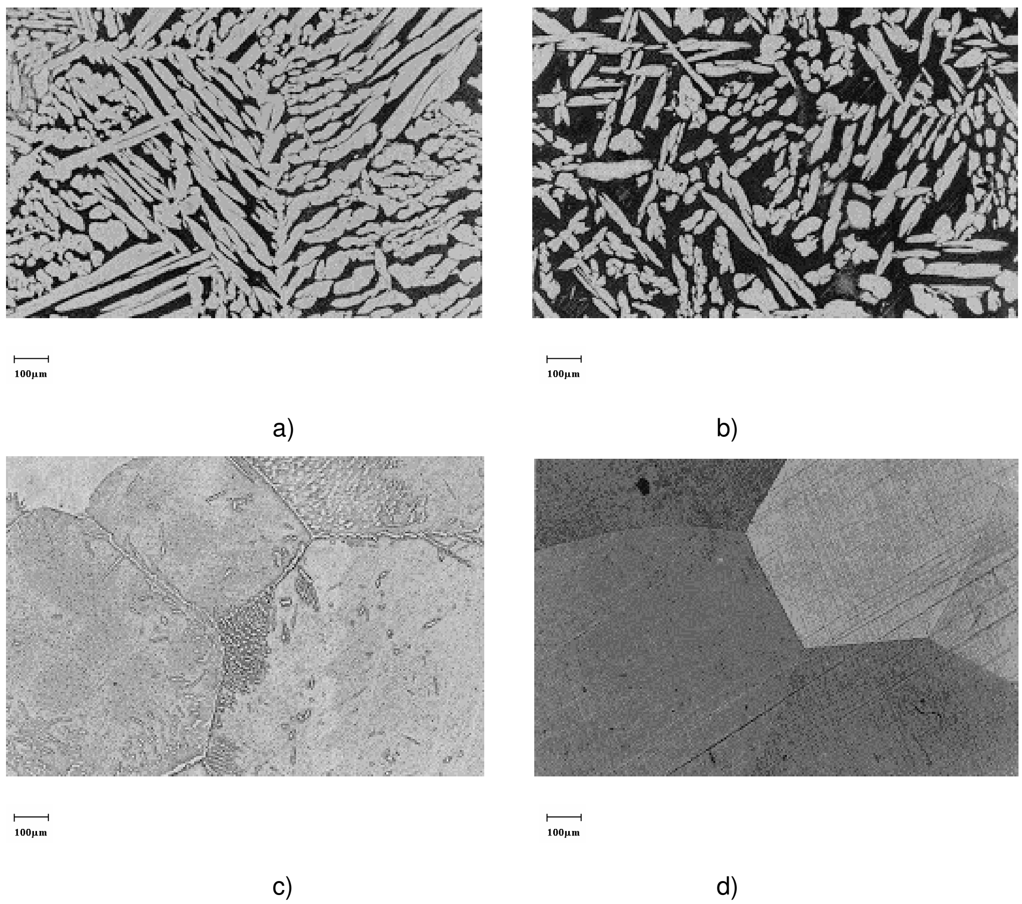


Figure 2 - Microstructure of as cast alloys with different Al contents (100X): a) alloy nº3 (0.49 wt.%Al), b) alloy nº4 (1.05 wt.%Al), c) alloy nº5 (1.60 wt.%Al) and d) alloy nº6 (3.37 wt.%Al).

Although alloys nº 3, nº 4 and nº 5 have a $\alpha+\beta$ brass microstructure, it is clear the influence of aluminium on decreasing the volume proportion of α phase as well as on the formation of a structure with 100% of β phase (alloy nº 6). For all the alloys reported in this work, the presence of γ phase was detected only in the sample of the alloy nº 10, both in cast conditions and subsequently to homogenization experiments.

The homogenization experiments at different temperatures allowed the evaluation of the influence of the temperature on equilibrium phases and its chemical compositions.

Using a regression analysis, of the results obtained in homogenization experiments, it has been possible to estimate several relationships that express the chemical compositions of the equilibrium phases at different homogenization temperatures, in the form of (%Zn) = A + B x $(\%Al)^2$ (equations 1 to 4 of the table 2 for α phase and equations 5 to 8 of the same table for β phase). On table 2 it is also presented the correlation coefficient (r^2) corresponding to each expression.

Table 2 – Expressions determined by regression analysis indicating the chemical composition of equilibrium phases at different homogenization temperatures in the form of (%Zn) = A + B x $(\%Al)^2$.

Temp (ºC)	**A**	**B**	**Uncertainty levels**	**r^2**	**Equation Nº**
650	36.99	- 2.94	± 0.67	0.87	1
550	37.62	- 2.47	± 0.96	0.88	2
450	37.61	- 1.82	± 0.75	0.89	3
350	37.67	- 1.91	± 0.90	0.86	4
650	42.35	- 1.93	± 0.65	0.93	5
550	43.75	- 1.74	± 0.76	0.96	6
450	44.75	- 1.33	± 0.68	0.97	7
350	45.81	- 1.38	± 0.89	0.96	8

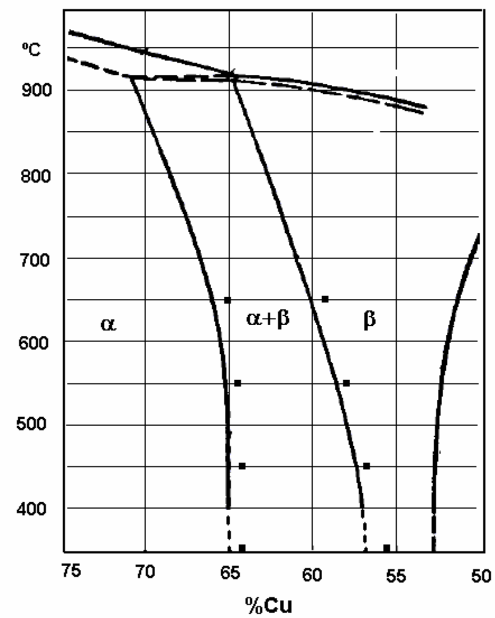
An overall multivariate analysis allowed to express the influence of the temperature on the equilibrium phases, equations 9 and 10, for the range of compositions studied:

$$\%Zn_{(\alpha)} = 35.29 - 2.06\ \%\ Al_{(\alpha)}^{2} + 1.25\ x10^{-2}\ T - 1.57\ x\ 10^{-5}\ T^{2} \pm 0.84 \qquad (9)$$

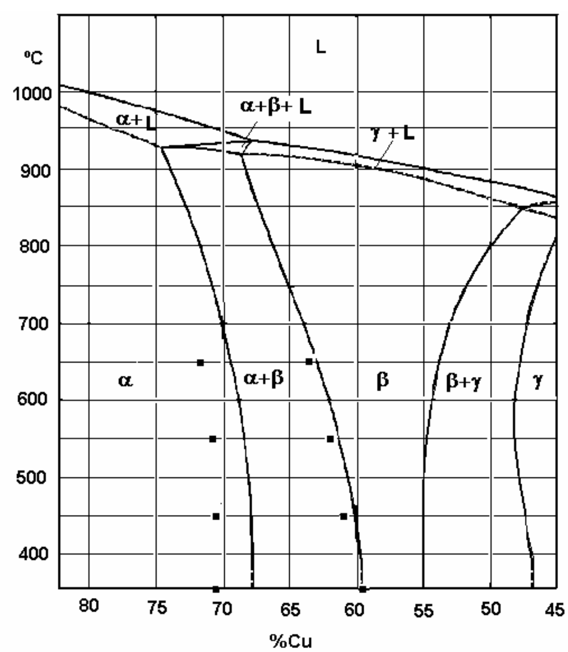
$$\%Zn_{(\beta)} = 50.53 - 0.66\ \%\ Al_{(\beta)} - 1.10\ \%\ Al_{(\beta)}^{2} - 1.25\ x\ 10^{-2}\ T \pm 0.81 \qquad (10)$$

with r^2 of 0.85 and 0.96, respectively.

Figure 3 compares the results obtained in this research with the existing phase diagram obtained in previous investigations [1932Bau].



a)1% Al



b) 2%Al

Figure 3 – Vertical sections proposed by Bauer *et al* for the Al-Cu-Zn system, for 1 and 2 wt% of aluminium content and for copper contents between ~45 and 90 wt.% [1932Bau], and calculated points obtained from expressions (9) and (10).

The results presented on figure 3 show that the results concerning the equilibrium region of $\alpha+\beta$ phase, are slightly different from the existing vertical sections available in the literature. For the vertical section of 1 wt.% of Al, figure 3a) both solubility limits of α and β phase are displaced for lower copper solubility than the obtained from Bauer and Hansen in previous studies [1932Bau]. This difference is more evident for the copper solubility in α phase. For 2 wt.% of Al, figure 3b), it was detected some differences which becomes also more evident for the solubility limit of copper in α phase. In this vertical section the solubility limits for both α and β phases are shifted to higher values of copper solubility than the obtained by previous works [1932Bau].

These differences may be explained by the less accurate experimental techniques used in previous works (thermal analysis and metallographic techniques), while in this work very accurate analytical methods like the XRF spectrometry and EPMA were employed.

Conclusions

The results obtained in this work enabled the establishment of several relationships that indicate the effect of aluminium content of brasses on the chemical composition of the equilibrium α and β phases, at different temperatures. The use of a more accurate technique to determine the chemical composition of the equilibrium phases, at different temperatures, may explain the differences with other published works. These results show that the solubility limits for copper in α and β phases could be different from the proposed for Bauer and Hansen. The range of temperatures covered in this research allowed also the determination of equilibrium data for the temperature of 350ºC, which was previously unknown.

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